

## Use of Titanium Dioxide Reaction for Degradation of Chlorophenol

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### ABSTRACT

The use of Titanium Dioxide (TiO<sub>2</sub>) reaction for degradation of Chlorophenol (CP) has been investigated. Initial TiO<sub>2</sub> concentration of 10 mg.L<sup>-1</sup> and 40 minutes of reaction time was enough to eliminate 100 mg.L<sup>-1</sup> of CP from the wastewater. The bio-treatability of the solution (BOD<sub>5</sub>/COD ratio) was improved from 0, for the untreated CP solution, to 0.18 (corresponding BOD<sub>21</sub>/COD was 0.24). The pre-treated solution biodegradability enhancement was verified by performing biological oxidation for the pre-treated solutions. The biomass used in aerobic digestion is fresh activated sludge from municipal wastewater treatment plant. More than 80% of the Total Organic Carbon (%TOC) elimination was obtained by co-digestion of the pre-treated solution with wastewater. The hydraulic retention times used in the bioreactors were of the same order of magnitude of those used at domestic wastewater treatment plants; i.e., between 12 and 24 hours. Kinetic studies based on pseudo-first order kinetics have also been carried out with the demonstration of constants to be ranged between 0.67 and 1.7 L.g TVSS<sup>-1</sup>.h<sup>-1</sup>.

**KEYWORDS:** Aerobic reactor, Biodegradability, Chlorophenol.

### INTRODUCTION

Chlorophenolic compounds are of wide use in the production of wood preservers, pesticides and biocides, and constitute an important class of recalcitrant pollutants (Xiangchun et al., 2003). They were reported in the waste of petrochemical industries, oil refinery, plastic, pulp, and insulation material (Raung, 1984; Liu et al., 1991; Heidi et al., 2004). These compounds cause serious environmental problems, due to their high toxicity, recalcitrance, bioaccumulation, strong odor emission, persistence in the environment and suspected carcinogenicity and mutagenicity (Contreras et al., 2003; Wang et al., 2000). Chlorophenol concentration in the groundwater from a contaminated aquifer was reported as high as 25–55 mg.L<sup>-1</sup> (Edgehill and Finn, 1982). In wastewater, the concentrations are higher than 200 mg.L<sup>-1</sup> (Ormad et al., 2001; Xiangchun et al., 2003). These findings illustrate the seriousness of chlorophenol

pollution and the importance of an effective method for treating chlorophenol-containing wastes.

In this study, chlorophenol (CP) was chosen as the target pollutant, because it has been found in many industrial effluents, and formed during manufacturing of herbicides (Antizar-Ladislao and Gali, 2003). CP can also cause a noticeable harm to human such as irritation of the respiratory system, damage of kidneys, liver and blood-forming organs (Standard Methods, 1985). Chloroaromatics were reported to have many side effects on skin adsorption (Miller et al., 1988).

In general, biological treatment of wastewater is often the most economical alternative when compared with other treatment options. However, if conventional biological treatment methods are used, microorganisms are easily inhibited by toxic compounds like chlorophenols (Yu and Hu, 1994; Hirvonen et al., 2000). Additionally, the biomass is easily lost from the system thus greatly reducing the treatment efficiency.

TiO<sub>2</sub> oxidation has been carried out successfully to mineralize many organic compounds. An important drawback of these AOPs (Advance Oxidation

Processes) is that their operational costs are relatively high (Ghaly et al., 2001; Jemenz et al., 2002; Kaczmarek et al., 2002; Farkas and Dekany, 2002; Contreras et al., 2001). As an economical way for treating bio-recalcitrant organic wastes, previous studies attempted some form of combination of the chemical oxidation with biological processes (Marco et al., 1997; Ledakowicz, 1998; Chamarro et al., 2001; Sarria et al., 2002; Ben Abderrazik et al., 2002; Oussi et al., 1997; Al Momani et al., 2002). Generally, the chemical process would be used as a pre-treatment in order to increase biodegradability and to remove toxicity of the wastewater (Pitter and Chudoba, 1991; Al Momani et al., 2001), while the biological process completes the

final mineralization of the organic matter (Scott and Ollis, 1995; Sarrià et al., 2002; Contreras et al., 2003).

The  $\text{TiO}_2$  photo-assisted system has received special attention as a potential wastewater treatment process. To date, there are a few works that explore the possible combination of this system with a biological oxidation step for the wastewater treatment (Pulgarin et al., 1999; Parra et al., 2000; Sarria et al., 2003). In this sense, this study attempts to fill this gap focusing on the mineralization of CP, through integrated processes.

Accordingly, the effect of the  $\text{TiO}_2$  process on biodegradability improvement of  $100 \text{ mg.L}^{-1}$  CP solution has been studied. The aerobic biological degradation of the pre-treated solutions has been tested.

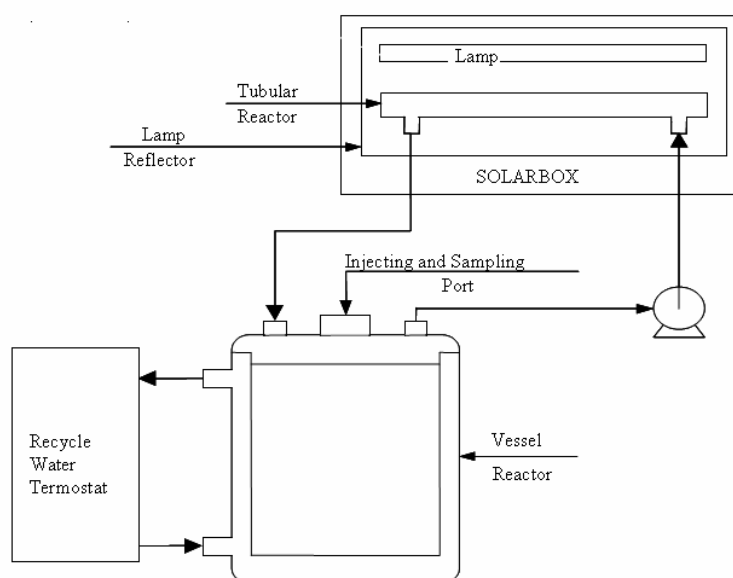


Figure 1: Experimental setup

## MATERIALS AND METHODS

### Reagents

The reagents used in the experimentation were: chlorophenol (>98%, Merck), sodium hydrogen sulphite solution (40% W/V, Panreac), uranyl nitrate (98%, Panreac), oxalic acid (99.5%, Panreac), potassium permanganate (99%, Probus), acetonitrile (99.8%, isocratic grade for HPLC, Merck), phosphoric acid (85.5%, Probus), potassium dichromate (99%, Probus), mercury sulphate (98%, Probus), silver sulphate (98%, Probus), sulphuric acid (95-98%, Fluka) and Millipore water (Milli-Q Millipore system with an  $18 \text{ M}\Omega\text{cm}^{-1}$

resistivity). Stock solutions and all reagents were prepared with millipore water.

### Analytical Methods

Chlorophenol concentration was followed by reverse-phase High Performance Liquid Chromatography (HPLC). A Waters HPLC apparatus (photodiode array detector 996, auto sampler 717 and controller 600) with Millennium software was used. The reverse-phase column used was a Spherisorb ODS2,  $5\mu$ ,  $25 \times 0.46 \text{ cm}$ . The mobile phase was a mixture of water, acetonitrile and phosphoric acid (60:40:0.5 %) isocratically delivered by a pump at a flow rate of 1

$\text{mL}\cdot\text{min}^{-1}$ . To assure result reasonability, the standard solution and the tested concentration measurements were repeated 3 times, obtained results were averaged, tested and gave as a maximum 5 % standard deviation of the mean value.

The Total Organic Carbon (TOC) was determined by a Dohrmann D-C-190 high temperature analyzer provided with an auto sampler. The precision in TOC measurements was in the range of  $\pm 1 \text{ mg}\cdot\text{C}\cdot\text{L}^{-1}$ .

Biological Oxygen Demand ( $\text{BOD} \pm 3 \text{ mg O}_2\cdot\text{L}^{-1}$ ) was measured according to the procedures explained in (Standard Methods, 1985), section 5210D by means of an oxitop system (VELP Scientific).

Chemical Oxygen Demand ( $\text{COD} \pm 3 \text{ mg O}_2\cdot\text{L}^{-1}$ ) was also followed as indicated in the (Standard Methods, 1985), section 5220D.

Analysis of Total Suspended Solids (TSS) and Total Volatile Suspended Solids (TVSS) was performed following the guidelines given by the (Standard Methods, 1985), sections 2540D and 2540E, respectively.

## Installations

### A) Photo-reactor

The experiments were carried out in a 5 L experimental device presented in Figure 1. The photo-reactor is equipped with germicides low-pressure mercury lamp, placed in its centre. The lamp with a total power of 40 W emits radiation basically at 253.7 nm.

The UV light intensity entering to the photo-reactor was measured periodically (each 100 irradiation hours) by chemical actinometry. Through the actinometry, the radiation fluxes entering the reactor, at the beginning and the end of experiments, were  $13.8 \pm 1.5$  and  $12.9 \pm 1.5 \mu\text{Einstein}\cdot\text{s}^{-1}$ , respectively.

### Procedure

All the experiments were carried out in batch mode, with a recirculation flow rate of  $100 \text{ L}\cdot\text{h}^{-1}$ . Experiments were performed at  $(21-25)^\circ\text{C}$  and atmospheric pressure. In each experiment,  $100 \text{ mg}\cdot\text{L}^{-1}$  of CP and  $40 \text{ mg}\cdot\text{L}^{-1}$   $\text{TiO}_2$  solutions were prepared with tap water. The solutions were perfectly mixed to guarantee that all CP was dissolved. The pH of the reaction solution was allowed to evolve freely. The photo-reactor was filled with the solution, and it was allowed to circulate for 5

minutes through a peristaltic pump. Then UV light was switched on immediately. The initial and final solutions from the reactions were directly used for COD and BOD determination.

### B) Biological Reactor

Aerobic biological oxidation was completed in two 1.5 L reactors, equipped with a magnetic stirrer and an air diffuser. The initial biomass for both reactors was sewage sludge coming from a municipal wastewater treatment plant located in Mutah (Jordan). The reactor biomass was fed during 4 weeks with municipal wastewater ( $\text{TOC} \approx 70 \pm 16 \text{ mg}\cdot\text{L}^{-1}$ ) obtained from the same treatment plant. During this time, the biomass concentration, measured as TVSS, was stabilized at approximately  $1 \text{ g}\cdot\text{L}^{-1}$  in both reactors.

### Bio-oxidation Procedure

After four weeks of start-up, the pretreated solutions were used as part of the feeding mixture. Before feeding the reactors, pre-treated solution pH was adjusted to 7.0 and nutrients, containing  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MgSO}_4$  and buffer solution, were added according to the procedure explained in (Standard Methods, 1985), section 5210D.

The reactors worked in semi-continuous stirred tank conditions, with hydraulic retention times compressed between 10 days and 12 hours. The percentage of pretreated solution in the feeding mixture was progressively increased.

## RESULTS AND DISCUSSION

### Biodegradability Improvement of CP

CP is not a readily biodegradable compound as it can be seen from BOD value ( $\text{BOD}_5$  and  $\text{BOD}_{21} = 0.0$ ). The use of low  $\text{TiO}_2$  concentration is advantageous for the following reasons:

- Higher  $\text{TiO}_2$  concentration in the reaction solution reduces the UV transmissivity and decreases the reaction rate.
- Fe (II) at a higher concentration may act as oxidative species scavenger (Murphy et al., 1989) and the overall reaction is decelerated.
- Low amounts of  $\text{TiO}_2$  avoid sludge precipitation and its subsequent separation when the treated solution is neutralized before the biological process.

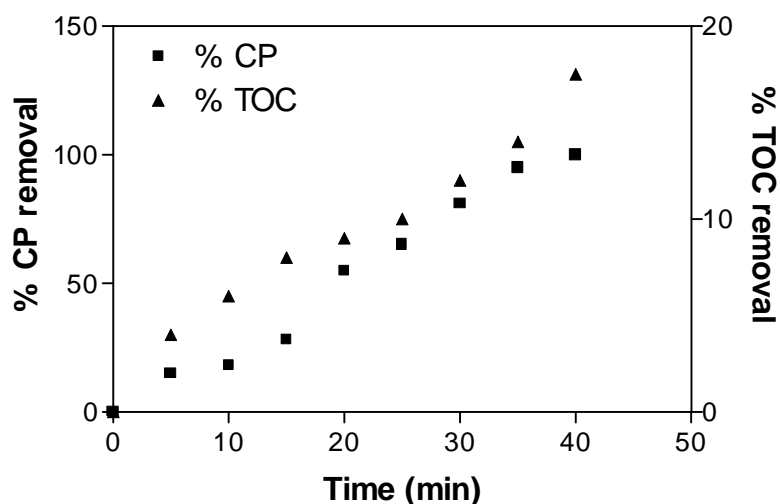


Figure 2: CP % removal and TOC % removal as functions of the reaction time

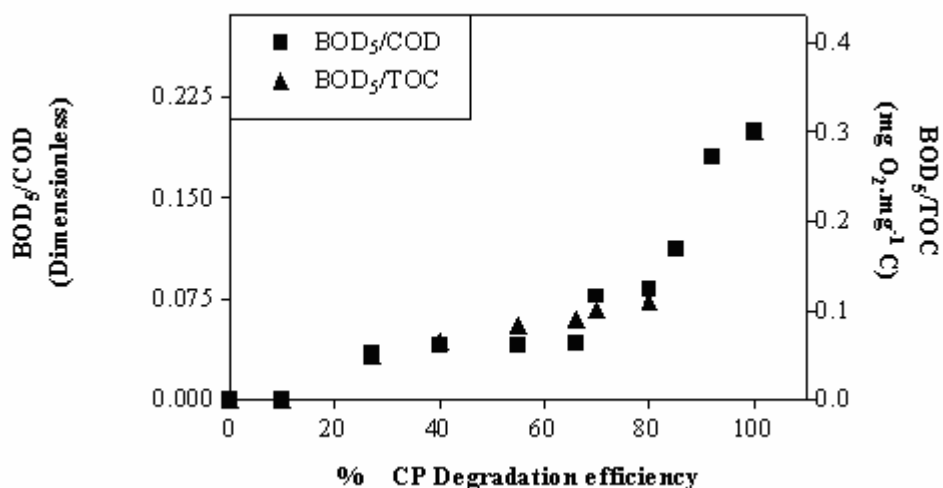


Figure 3: The evolution of BOD<sub>5</sub>/COD and BOD<sub>5</sub>/TOC as functions of % CP degradation efficiency

Figure 2 presents CP removal efficiency and total organic carbon elimination efficiency as functions of the reaction time. The reaction is considered one of the most powerful oxidants used in water treatment. It was observed that the CP degradation rate depended on the reaction progress. All CP was degraded (100 % CP degradation efficiency) when TiO<sub>2</sub> used was at a concentration of 10 mg.L<sup>-1</sup>. At this condition, Total Organic Carbon (%TOC) elimination was decreased by 17.5 %.

The biodegradability of the pre-treated solutions was followed throughout the experiments. Figure 3 shows the BOD<sub>5</sub>/COD and BOD<sub>5</sub>/TOC ratios evolution as a function of CP removal efficiency. BOD<sub>5</sub>/COD and

BOD<sub>5</sub>/TOC ratios started to increase as the remaining concentration of CP in the solution decreased. A considerable improvement on biodegradability was observed at the point where more than 75% of the initial CP was removed. When all CP had been eliminated (100% degradation efficiency), the BOD<sub>5</sub>/COD and BOD<sub>5</sub>/TOC of the solution were 0.2 and 0.40, respectively. Obtained results may suggest that some of the primary intermediates of CP are not easily biodegradable or need more oxidation to increase their biodegradability. In general, a BOD<sub>5</sub>/COD ratio between 0.3 and 0.4 is considered as a cut-off limit between biodegradable and hard biodegradable effluent (Metcalf and Eddy, 1985).

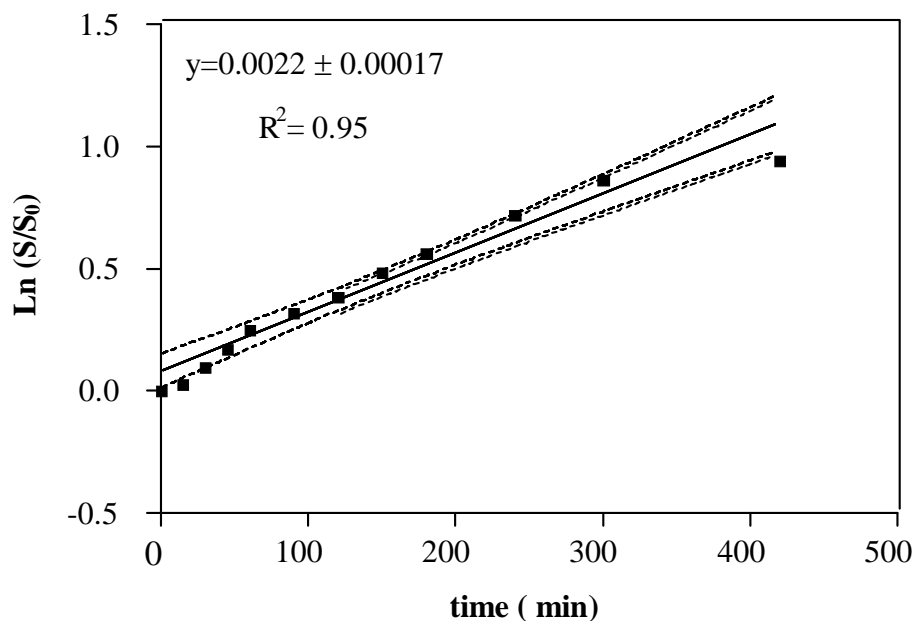
**Table 1: CP bio-oxidation results at different feed ratios and different HRT values**

Feed <sup>(1)</sup>	HRT (days)	OLR (mg.C.L <sup>-1</sup> .day <sup>-1</sup> )	TOC <sub>i</sub> (mg.C.L <sup>-1</sup> ) <sup>(2)</sup> (n° of samples)	TOC <sub>f</sub> (mg.C.L <sup>-1</sup> ) <sup>(2)</sup> (n° of samples)	TOC %
15/80	10	25	30 (2)	12.4 (2)	58.6
20/80	5	46	39 (4)	12.7 (4)	67.6
20/80	2	98	45 (5)	11.8 (5)	73.7
30/70	2	44	45.8 (5)	9.6 (5)	79
50/50	2	64	67.5 (5)	14.6 (6)	78.4
70/30	2	150	76.6 (5)	14.9 (5)	80.5
100/0	2	23	21.8 (7)	10.2 (7)	44
100/0	1	38	28.2 (10)	10.8 (10)	61.5
100/0	0.5	70	29.4 (10)	13.0 (10)	55.8

(1) % pre-treated solution to wastewater.

(2) Error has been calculated for 95% confidence level.

Numbers in parentheses correspond to the number of samples used in calculation; the average result has a 95% confidence level error.



**Figure 4: Kinetic fitting of bio-oxidation of pre-treated solution in biological reactor (HRT=12 hours, feed 100% pre-treated solution, T=23±2 °C, pH=7.0±0.4, V<sub>r</sub>=1.5 L and TVSS=0.13 g/L)**

#### ***Aerobic Biological Oxidation***

Based on photo oxidation results and the data related to biodegradability improvement, it was decided to use, in feeding the bio-reactors, the pre-treatment solution with CP degradation efficiency of 100% (corresponding to a BOD<sub>5</sub>/COD ratio of 0.18). Under these conditions, total organic carbon concentration of pre-treated solution was around 32 mg C.L<sup>-1</sup>. The reactor was fed a mixture of CP pre-treated solution and municipal

wastewater. The amount of CP pre-treated solution and hydraulic retention times (HRT) were varied. To start with, the concentration of treated solution was 20 V/V % (i.e., 20% V/V CP pre-treated solution and 80% municipal wastewater), the amount was increased progressively until the reactors' feed was 100 % CP pre-treated solution. HRT was also decreased gradually; starting with 10 days and decreased to 12 hours.

**Table 2: Kinetic constant values ( $K_0$ ) for bio-reactor at different pre-treated solution percentages and different HRTs**

Reactor	HRT	$R^2$	X (g TVSS.L <sup>-1</sup> )	$K_0$ (L.gTVSS <sup>-1</sup> .h <sup>-1</sup> )
Bio-reactor fed 100% pre-treated solution (number of samples)	1 day	0.96	0.13 (4)	0.78
	12 h	0.98	0.13 (2)	1.02

Table 1 summarizes the results obtained in both biological reactors. Results include initial Total Organic Carbon ( $TOC_i$ ) after feeding the reactor (i.e., at the beginning) of bio-oxidation cycle, final Total Organic Carbon ( $TOC_f$ ) (i.e., at the end of biooxidation cycle), Total Organic Carbon (%TOC) elimination and the Organic Loading Rate (OLR). Experimental results were recorded after the reactor was assumed to be under steady state conditions. All working conditions gave average total organic carbon elimination values higher than 50%. When biological reactor feed was 70 % of CP pre-treated solution and 2 days HRT; TOC elimination was 80.5% .

### Kinetic Study

Monod (1949) model has been the most widely used one to describe the processes of biological degradation of compounds in wastewaters. If one of the essential requirements (substrate and nutrients) for bacterial growth were present in limited amounts, it would be depleted first and growth would cease. Assuming that the intermediates formed in the pre-treatment step follows a Monod model and the organic matter removal follows first-order kinetics (as the treated solution is a multi-component system, i.e.,  $K_s \gg S$ ) (Chudoba, 1990), the biological reactor kinetics could be described by:

$$-\frac{1}{X} \frac{dS}{dt} = \frac{kS}{(K_s + S)} = K_0 S \quad (1)$$

where  $K_0$  is the pseudo-first order kinetic constant (L.g<sup>-1</sup> VSS. hr<sup>-1</sup>),  $S$  is the concentration of growth-limiting substrate in the solution, here presented as dissolved organic carbon (TOC), [mgTOC.L<sup>-1</sup>] and  $K_s$  the Monod semi-saturation constant [mgTOC.L<sup>-1</sup>]. If Eqn. (1) is integrated with the initial condition  $S=S_0$  for  $t=0$ , the result is

$$\ln\left(\frac{S_0}{S}\right) = K_0 t \quad (2)$$

According to Eqn.(2), a plot of  $\ln(S_0/S)$  versus time must lead to a straight line. Figure 4 shows the plot obtained for the bioreactor operated with CP pre-treated solution with a degradation efficiency of 100% and 12 h HRT (calculations were performed with 95% confidence level, dashed line in the figure). A good correlation of the experimental points to a straight line ( $R^2 > 0.95$ ) confirms the validity of the proposed model. Table 2 provides the  $K_0$  values for both reactors working at 100% of pre-treated solution and HRTs of 12 and 24hr (between brackets, samples' numbers). Beltran et al. (2000) and Contreras et al. (2003) have studied the aerobic bio-degradation of phenolic and chlorophenolic solutions pre-treated by AOP's. The reported kinetic values are in agreement with the values obtained in this study.

Moreover, it was observed that the rate constant at an HRT of 12 hours is faster than that at an HRT of 24 hours. The obtained tendency may aim to the way the reactor was fed. The bioreactor was operated for 11 cycles at an HRT of 24 hours and then 8 cycles at an HRT of 12 hours. The kinetic study, at each HRT, was performed during the last three cycles. Thus, more biomass acclimation can be expected for an HRT of 12 hours than for an HRT of 24 hours.

### CONCLUSIONS

Data obtained from the TiO<sub>2</sub> treatment demonstrated that the biodegradability, measured as BOD<sub>5</sub>/COD, was increased from 0 up to 0.2 (BOD<sub>21</sub>/COD = 0.44). The most considerable enhancements in BOD<sub>5</sub>/COD ratios were obtained when all CP had been depleted from the solution. At the same conditions, the mineralization of organic carbon was 17.5% and the average oxidation state was found to be 1.32.

Pre-treated solutions were biologically oxidized in two semi-continuous stirred tank reactors containing

fresh activated sludge obtained from municipal wastewater treatment plant. The results indicate that after pre-treatment, co-digesting the pre-treated solution with municipal wastewater, more than 82 % of TOC elimination can be achieved by aerobic bio-oxidation. The bio-reactor was operated in conditions similar to the operational conditions used in municipal wastewater plants (HRT values of 12 hours and 48 hours). A kinetic study based on the simplified pseudo-first order kinetic

model was conducted. Constants for CP pre-treated solution were found to be in the range of 0.67-1.7 L.g TVSS<sup>-1</sup>.h<sup>-1</sup> for both reactors.

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## Nomenclature

BOD <sub>5</sub>	Five days biological oxygen demand [mg O <sub>2</sub> . L <sup>-1</sup> ]
COD	Chemical oxygen demand (mg O <sub>2</sub> .L <sup>-1</sup> )
HRT	Hydraulic retention time (days)
K <sub>o</sub>	First order kinetic constant [L (g VSS.h) <sup>-1</sup> ]
K <sub>s</sub>	Monod semi-saturation constant [mg TOC.L <sup>-1</sup> ]
OLR	Organic loading rate [mg C. L <sup>-1</sup> .day <sup>-1</sup> ]
S	Biodegradable substrate concentration [mg TOC. L <sup>-1</sup> ]
TOC <sub>f</sub>	Final total organic carbon [mg C.L <sup>-1</sup> ]
TOC <sub>i</sub>	Initial total organic carbon [mg C.L <sup>-1</sup> ]
TOC%	%Total organic carbon elimination
X	Biomass concentration [g VSS. L <sup>-1</sup> ]

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